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INFRARED SPECTROMETRY OPTIONS WITH ATR METHOD FOR OXIDATION EVALUATION OF OILS

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Research article

Abstract: Theme Article deals with the use of infrared spectrometry (ATR method) to analyze oxidation, because oxidation plays a role in the self-ignition of oils. As samples were used - sunflower oil, linseed oil. Aim experiment to verify that the infrared spectrometry modified by the ATR method is suitable for the evaluation of the oxidation of liquid substances. Verification of the suitability of the method was performed by comparing the data obtained during the measurement of this experiment with the data verified in other publications. Subsequently, the influence of temperature and time on the oxidation assumed was investigated.

Keywords: Oxidation, linseed oil, sunflower oil, ATR.

Introduction

In today's world, optical methods are used in every industry, perhaps. In the health, agriculture, food, Engineering Etc. Optical methods provide us with crucial information on the substances examined. For example, chemical composition of the substance, its chemical and physical properties. These methods are numerous and their use is inexhaustible. They can examine substances at atomic level. The reason is that these methods are called optical is that previously, a visible component of electromagnetic radiation was used for the analysis. (Čablík et al., 2006)

Optical methods differ from other analyses in that the measuring instruments are constructed of optical elements (prisms, lenses, lattice....). And also by examining the optical properties of the substances analysed and the radiation itself. These methods use electromagnetic radiation (current of particles, waves - electrons, photons, which have varying kinetic energy). (Čůta, 1986)

Materials and methods

The essence of the method and its spectrum

Attenuated Total Reflectance or ATR is now the most widespread used FTIR attachment. The ATR generally allows qualitative or quantitative analysis of samples with little or no preparation of the sample, which considerably speeds up the analysis of the sample. The main benefit of the ATR analysis comes from the very thin depth of penetration of the infrared beam into the sample. This is in the opposite of the traditional FTIR analysis, when the sample must be formeded into pellets or presseded into a thin film, before analysis to prevent the complete absorption of belts in the infrared spectrum. (ATR, 1999).

Analyzed test substance is coated on the surface of the crystal, which is permeable to infrared radiation. These crystals are made of different materials (e.g. Sapphire, Diamond...). The infrared beam must penetrate the crystal at a certain angle to ensure full reflection on the upper and lower sides of the crystal. The beam permeates the crystal all the way to the opposite end, where the beam leaves the crystal. The beam is partially penetrated into a very small sample layer. Thus the beam is changed and the infrared spectrum of the examined substance is created. (ATR, 1999).

This technique can be measured as Fixed and liquid samples. But solid samples must ensure good contact with the crystal. This limits the method just to the surfaces of solid samples. If we wanted to analyze the sample whole and in whole, we would have to choose another method. Because ATR cannot examined substance into deep. (ATR, 1999).

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Use of ATR

This method can be measured similar to the infrared spectrometry of a functional group, the binding of chemical substances. It can also analyse the substance surface composition. It can detect changes in the structure of the substance, thus it is also suitable for observing various chemical reactions such as oxidation. (Johansson et al., 2005)

Influencing measurements

ATR is influenced by various factors (e.g. wavelength of infrared radiation, refractive index, ATR shape Crystal...). (ATR, 1999)

Refractive index - The condition of the emergence of total reflection is that the angle of impact will be greater than the critical angle. A just critical angle is defined by the refractive index of the sample and the crystal. (ATR, 1999)

ATR Crystal shape - we distinguish the shape of the crystal and the numbers of reflections of the ATR crystals on the one-reflective and many-reflective. (ATR, 1999)

Contact of the sample and the ATR crystal - as this method takes a very thin part of the substance to be examined, excellent contact between the crystal and the examined substance must be ensured. (ATR, 1999)

The composition of the ATR crystal - several factors play a role here. Refractive Index, infrared radiation permeability, but also the chemical structure of the crystal itself. (ATR, 1999)

Device type and specifications

For infrared spectrometry measurement, a Nicolet iS 10 FTIR spectrometer was used. In general, the task of all infrared spectrometers is to record the infrared spectrum (dependence of radiation intensity on the wavelength). The FTIR spectrometer converts the wavelength from the infra-red area into the audio frequency domains (kHz), where detectors are eligible to register both the wavelength and its intensity. Nowadays, there is no designed infrared spectrometer to register wavelengths in the respective range and at the same time the intensity of radiation for each wavelength. (Manual FTIR, 2006).

Properties and oxidation of samples

Vegetable oils consist of mixtures of triacylglycerols of different fatty acids. These fatty acids are represented by carbon chains of different lengths and varying degrees of unsaturation. Besides triacylglycerols, mono and diglycerides, alicyclic alcohols, free fatty acids, fat soluble vitamins and terpenes also appear in vegetable oils. What matters, too, is the combination of individual fatty acids in molecules of triacylglycerols. For example, the least probable occurrence of acids is in the form of simple triacylglycerols. Most typically, the esterification of the glycerol secondary hydroxyl group is carried out by the 18 carbon-chain. This site is less susceptible to oxidation in the glycerol molecule. For the remaining two hydroxyl groups, esterification with saturated and unsaturated acids occurs randomly. (Hájek et al., 1998)

Vegetable oils are generally easily oxidized and autooxidized due to the presence of unsaturated bonds in fatty acid chains. The result is the cleavage and decomposition of organic acid molecules. The oxidation occurring in vegetable oils is the sum of chain reactions of the radical mechanism. (Hájek et al., 1998)

Initiations:

$$R\text{-}H = R \bullet + H \bullet$$

Propagation:

$$R\bullet + O2 = RO2 \bullet$$

$$RO2 \bullet + R\text{-}H = R\text{-}O\text{-}O\text{-}H + R \bullet$$

Termination:

$$2R \bullet = R\text{-}R$$

$$R \bullet + RO2 \bullet = R\text{-}O2\text{-}R$$

$$2RO2 \bullet = R\text{-}O2\text{-}R + O2$$

The Production of free radicals in the range of diene and polyene aliphatic compounds is often accompanied by isomerization and rearrangement. Radicals formed during the autooxidation formation of peroxides, or formed by the breakdown of these peroxides, have the ability to form oligomeric and polymeric products. That is, they are involved in the chain reaction of unsaturated fatty acids. In the case of vegetable oils, this reaction leads to the formation of a polymer network (used, for example, in ferments as a thin protective film). (Hájek et al., 1998)

Oxidation of oils generally depends on the oxidation conditions and the type of oil. Autooxidation products at room temperature - hydroperoxides, aldehydes and alcohols. Further, ketones, lactones, furan, fatty acids, water, and many others are formed. (Vlachos et al., 2006)

It is known that oxidation of vegetable oils (predominantly ferments), linoleate and linolenate structures are rapidly oxidized because they

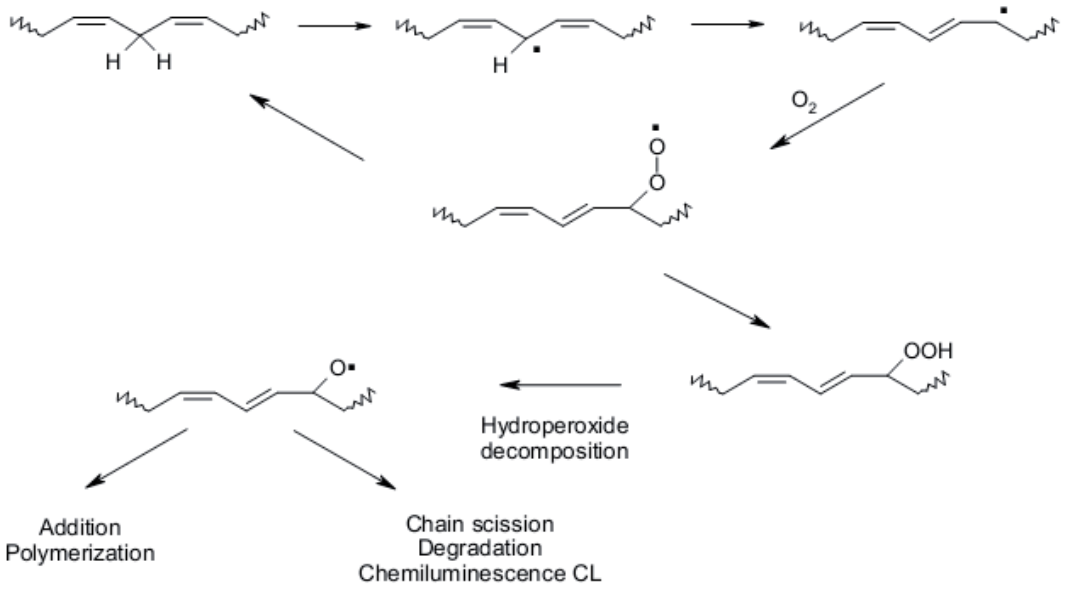

Fig. 1 Schematic description of auto-oxidation for the linoleate structure (decomposition of hydroperoxide results in a cleavage or addition reaction) (Johansson et al., 2005)

contain double allylic hydrogen atoms. When the hydroperoxides formed decompose, they form substances that either amplify (cross-link) the system or cause chain cleavage. Optimal oil suitable for protective coatings will contain reactive groups that promote crosslinking, rapid reaction, and leave low residual unsaturated bonds to allow long lasting durability of the final coat. Fig. 1 is a schematic representation of the auto-oxidation of the linoleate structure. Decomposition of the hydroperoxide results in either an addition or cleavage reaction. (Johansson et al., 2005)

Some steps could lead to substance decomposition and subsequent photon emission, generally referred to as chemiluminescence (CL). One proposed mechanism is a couple of two peroxide radicals (ROO •) to form tetraoxides (ROOOOR) which, when decomposed, results in the emission of photons, and this is called the Russell mechanism. Another mechanism offers the possibility that hydroperoxide degradation (ROOH) generated in autooxidation may produce alkoxy radicals (RO •) Or similar reactive forms which in the second step will lead to the cleavage of the β-cleavage chain followed by photon emission. (Johansson et al., 2005)

Also, there is cis-trans isomerism and conjugation of the double bonds in the hydroperoxides formed. (Johansson et al., 2005)

The oxidation rate and propagation of the formed products depends on the time, temperature of the oxidation, the presence of antioxidants, the fatty acid composition, the degree of unsaturation, but also the origin of the seeds. (Johansson et al., 2005)

Samples used

The sunflower oil was first analyzed. The oil was refined, with no added substances (no antioxidants). For the purpose of the experiment, the oil was heat treated in several ways. Two Batches were given in thermostat and heated to 60 °C in a silicone bath. From there, samples were taken from thermostat to measure after 18 days and after 36 days. The third batch was placed in the refrigerator and kept at 4 °C. From refrigerator, samples were taken to measure after 18 days. The same procedure was used for linseed oil. (Kopřivová, 2016)

Results

Analysis of samples

Oil analyzes took place in three differently heat-treated versions of sunflower oil and a female. To see if different levels of oxidation have taken place (whether the effect of temperature and time on the oxidation process is demonstrated). By comparing the spectra in certain peaks, information on

the course and degree of oxidation can be obtained. If the size of the given peaks would change (would grow, diminish or a new peak would be created). Prior to measuring, the ATR diamond surface had to be washed with alcohol on a paper towel (to prevent degradation of impurities). Then the background of the OMNIC 8 spectroscopic software was measured. This is due to the sudden and unexpected deviations of spectra of the same samples (on the background spectrum, we know whether there was no contamination of the surface of the diamond, sample, etc.). Sample measurement was set to the average of 64 measured spectra. The instrument measures 64 spectra and then averages it into one final spectrum (this takes about two minutes). The resulting spectrum has to be saved manually because the software does not automatically save the data and the measured spectrum would be deleted. A sample of the original sunflower oil was then picked up with a plastic pipette and then transferred to the surface of the diamond. The amount applied to the surface of the diamond could be equivalent to two drops. Subsequently, the measurement spectra of the sample was started. After the measurement, which took about two minutes, the spectrum had to be stored. The oil was then removed from the diamond and the diamond surface cleaned with alcohol. This procedure was repeated two more times. Subsequently, the pipette used had to be replaced with a clean pipette (to avoid mixing of different temperature samples). (Poledník, 2016)

The next phase of the analysis was the evaluation of the resulting oil spectra. At first, the most similar spectra had to be selected and OMNIC 8 software averaged. (Poledník, 2016)

Subsequently, the spectra of different heat-treated samples were compared (to what extent the diameters are dissimilar). But those parts of the spectrum that were the most different had to be found manually because the OMNIC 8 software does not have such a feature. (Poledník, 2016)

Code names of oils samples:

- sunflower oil kept in the refrigerator- original sunflower oil;
- sunflower oil kept in the thermostat for 18 days - sunflower oil 18;
- sunflower oil kept in the thermostat for 36 days - sunflower oil 36;
- linseed oil kept in the refrigerator- original linseed oil;
- linseed oil kept in the thermostat for 18 days - linseed oil 18;
- linseed oil kept in the thermostat for 36 days - linseed oil 36. (Poledník, 2016)

The following tab. 1 contains the areas (in cm^{-1}) of spectra in which the biggest differences were between compared oils. (Poledník, 2016)

Tab. 1 Data from comparison of oils (Poledník, 2016)

Compared samples	**Areas [cm^{-1}]**				
Original linseed oil vs linseed oil 18	3514-3080	3514-3080	1825-1778	1705-1483	1365-1313
Sunflower oil vs sunflower oil 18	4000-3960	3539-3116	2595-2399	2252-1790	1675-1485
Original linseed oil vs linseed oil 36	3408-3190	2625-2403	2300-1973		
Original sunflower oil and sunflower oil 36	3410-3150	2610-2395	2258-1915	997-972	

The following table number 2 contains data from the previous four tables. These are compared with the data from the article, which contains the determination of the belts in which oxidation occurs. (Poledník, 2016)

To simplify labeling:

- Comparison of the original linseed oil and linseed oil 18 as linseed oil I;
- Comparison of original linseed oil and linseed oil 36 as linseed oil II;
- Comparison of original sunflower oil and sunflower oil 18 as sunflower oil I;
- Comparison of original sunflower oil and sunflower oil 36 as sunflower oil II. (Poledník, 2016)

Tab. 2 Comparing the values of this experiment with the values published in the past (Poledník, 2016)

Stacked Samples	**3800-3200 [cm^{-1}]**	**3050-2800 [cm^{-1}]**	**1800-1500 [cm^{-1}]**	**1000-900 [cm^{-1}]**
Linseed oil I	3514-3080	X	1705-1483	X
Linseed oil II	3408-3190	X	X	X
Sunflower oil I	3539-3116	X	1675-1485	X
Sunflower oil II	3410-3150	X	X	997-972

(The large X in the table indicates that there have been no significant changes in the areas).

3800-3200 cm^{-1} - belt of OH valency vibration.

3050-2800 cm^{-1} - belt of reducing valency vibration intensity.

1800-1500 cm^{-1} - belt of increasing intensities of carboxylic acids.

1000-900 cm^{-1} - belt of increasing trans-double bond intensity.

(Johansson et al., 2005; Hájek et al., 1998; Vlachos et al., 2006)

From table No. 2 follows that changes in certain strips of oxidation in both linseed oil and sunflower oil have indeed taken place. But that still does not prove the presence of oxidation. (Poledník, 2016)

In each averaged spectrum, the highest peak in the oxidized area had to be identified. Determine its wavelength and absorbance (peak height). This was done with all averaged spectra. (Poledník, 2016)

The following tables describe the absorbances and wavelengths of the highest peak peaks in the oxidized range of the spectrum (Tab. 3 and 4). Tab. 5 and 6 show the comparison of the highest peaks of variously heat treated oils in order to determine whether there has been a change. (Poledník, 2016)

Tab. 3 Wavenumbers and absorbances of the highest peaks in the oxidized area of linseed oils. (Poledník, 2016)

Samples	Wavenumber [cm^{-1}]	Absorbance
Original linseed oil	3468.12	0.00029
	1653.13	0.0017
Linseed oil 18	3470.32	0.00024
	1692.29	0.0055
Linseed oil 36	3502,46	0,00045
	1701.62	0,00045

Tab. 4 wavenumbers and absorbances of the highest peaks in the oxidized area of sunflower oils (Poledník, 2016)

Samples	Wavenumber [cm^{-1}]	Absorbance
Original Sunflower oil	3467.78	0.00009
	1653.04	0.00150
Sunflower oil 18	3467.93	0.00011
	1657.21	0.00100
Sunflower oil 36	3467.93	0.00011
	1653.01	0.00120
	984.72	0.00050

The following tab. (5 and 6) compared the highest peaks of different heat-treated oils. Below the columns are the wavenumbers and absorbances values of the highest peak. Each line represents the highest peak of each measurement, and it is then compared to the area for other measurements. To show whether the peak has grown, diminished, shifted, or not shown. It is not possible to compare different peaks at different positions. (Poledník, 2016)

Tab. 5 Data from the highest peaks in the wavenumber area of linseed oil (in the measurement column the wavenumber (left) and peak height (on the right)) (Poledník, 2016)

Oxidizing strips [cm^{-1}]	Original linseed oil	
3500-3200	Wavenumber [cm^{-1}]	Absorbance
	3502.10	0.00021
	3468.12	0.00029
1800-1500	X	X
	1653.13	0.00170
	Linseed oil 36	
3500-3200	3502.46	0.00045
	X	X
1800-1500	1701.62	0.00090
	1653.00	0.00260

Tab. 6 Data from the highest peaks in the wavenumber area of sunflower oil (in the measurement column the wavenumber (left) and peak height (on the right)) (Poledník, 2016)

Oxidizing strips [cm^{-1}]	Original Sunflower oil	
3500-3200	Wavenumber [cm^{-1}]	Absorbance
	3467.78	0.00009
1800-1500	1653.04	0.00150
1000-900	X	X
	Sunflower Oil 36	
3500-3200	3466.58	0.00012
1800-1500	1653.01	0.0012
1000-900	984.72	0.0005

(The large X in the tables indicates that the peak does not occur in the given area)

Thanks to this comparison, it was intended to assess the influence of temperature and time on the course of the expected oxidation. If the height of peaks changes in the same positions, for differently heat treated samples, it can be said that the expected oxidation of oils depends on temperature and time. Which is inconclusive in this case. Because differences in the measurement of the oils left in the thermostat for 18 days compared to the rest of the measurement were very small to none. In addition, changes in the peaks examined may not be due to oxidation. (Poledník, 2016)

In order to verify whether the oxidation really took place in the samples, it was necessary to take into account the specific peaks determined in similar experiments performed and published in the literature. (Poledník, 2016)

Thus, peaks with a wavelength of 3447 cm^{-1} and 3009 cm^{-1} were examined. Peak 3447 cm^{-1} belongs to O-H valency vibration of hydroperoxides. When oxidation hydroperoxides arise, so this peak should be enlarged (in case of temperature used in the thermostat). Peak 3009 cm^{-1} belongs to C-H valency vibration of CIS double bonds. There is a cis trans isomer. Disappear cis double-bonds and are replaced by a trans configuration. It is also associated with the emergence of hydroperoxides (the mechanism of lipid oxidation under moderate conditions). This peak is logically reduced. (Johansson et al., 2005; Hájek et al., 1998; Vlachos et al., 2006)

In the following tables (7 to 8), peaks of 3447 cm^{-1} and 3009 cm^{-1} of the original oils and oils 36 are compared. (Poledník, 2016)

Tab. 7 Data from a comparison of selected peaks in the area of the original linseed oil and linseed oil 36 (Poledník, 2016)

Original linseed oil		**Linseed oil 36**	
Wavenumber [cm^{-1}]	**Peak height**	**Wavenumber [cm^{-1}]**	**Peak height**
3447.13	0.00010	3446.93	0.00019
3009.99	0.0233	3009.73	0.02320

Tab. 8 Data from a comparison of selected peaks in a given area of the original sunflower oil and sunflower oil 36 (Poledník, 2016)

Original Sunflower oil		**Sunflower Oil 36**	
Wavenumber [cm^{-1}]	**Peak height**	**Wavenumber [cm^{-1}]**	**Peak height**
3447.00	0.00014	3446.87	0.00006
3008.36	0.01920	3008.34	0.01770

Tab. 7 to 8 show that the oxidation took place in the linseed oil, whereas the sunflower oil did not. (Poledník, 2016)

Discussion

Measurement evaluation

After comparing the data obtained from the oil measurements from this experiment, with the data from previous published experiments, it is possible to say that the oxidation in the linseed oil was carried out. Oxidation in sunflower oil, but did not take place. This could be due to, for example, that the warm-up temperature in the silicon bath was not high enough or that the oxidation of the samples was carried out only in an oxidation environment and the samples were not bubbling with the oxygen. Of course, the measured data results in some changes before and after the heating of the sunflower oil, but it could be attributed to thermal changes in the structure of the samples, not the oxidation. The results of this experiment are a little different with the results of published experiments, but it can be caused by different laboratory conditions, different samples, different preparation of the samples (this experiment focused on finding hydroperoxides and you need a lower temperature before they start decomposed), other types of measuring instruments (that means another code designation or other manufacturer). Why did linseed oil oxidation take place and not for sunflower oil? Both oils have a very similar composition, but linseed oil is used as a protective layer for wood. Therefore, it must have fast drying properties, In addition, it may contain various additives to improve the properties of the paint. (Poledník, 2016)

Conclusion

Oxidation in linseed oil has been proven. However, oxidation in sunflower oil has been not (the size of the sunflower oil 36 peak did not increase but decreased compared to the original sunflower oil, this phenomenon is not evidence of oxidation-table 8). Positive properties of the method ATR are -high speed of measurement, easy operation, the need for a small number of samples, easy and quick cleaning of the device. The infrared spectrometry modified by the ATR method is suitable for the evaluation of oxidation of linseed oil. For the evaluation of the oxidation of sunflower oil is inconclusive in this experiment.

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